

PATENT SPECIFICATION

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(54) DYEING COMPOSITIONS CONTAINING QUATERNARY AZO DYESTUFFS DERIVED FROM 2-AMINOPYRIDINE

(71) We, L'OREAL, a French Body Corporate of 14, Rue Royale, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

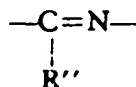
In our British Patent Specification No. 1,360,562 we describe and claim a composition suitable for dyeing human hair which comprises an aqueous or aqueous-alcoholic solution having a pH between 3 and 8 and containing 0.001 to 0.5% by weight of at least one diazamerocyanine or salt of a diazamerocyanine, of the formula



in which A represents a nitrogen-containing heterocyclic structure with 5 or 6 ring members, of the formula



wherein R denotes a lower alkyl radical (i.e. containing from 1 to 4 carbon atoms) or an optionally substituted phenyl radical, X denotes (i) an oxygen atom or a sulphur atom or a NR' radical, wherein R' represents a lower alkyl radical, (ii) a —CH₂— radical optionally substituted by one or two lower alkyl radicals or (iii) an ethylenic radical or a

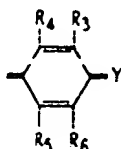


radical, wherein R'' denotes a hydrogen atom or a lower alkyl radical;

Z represents an ethylenic radical or a —NR''' radical, wherein R''' denotes a lower alkyl radical;

R₁ represents a hydrogen atom, a lower alkyl radical or phenyl radical, and R₂ represents a hydrogen atom or a lower alkyl radical, or R₁ and R₂ together with the carbon atoms to which they are bonded form a fused benzene ring optionally substituted by one or more halogen atoms or alkyl, alkoxy or nitro radicals,

B represents, *inter alia*, a nitrogen-containing heterocyclic structure with 5 or 6 ring members, which can contain other hetero-atoms and which may be one defined under A but which is not identical to A, or a ring of the formula



R'_2 denotes a hydrogen atom, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms, preferably methyl, ethyl or β -hydroxyethyl, or phenyl;

R'_3 and/or R'_4 represent a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, preferably methyl, or an alkoxy group of 1 to 4 carbon atoms, preferably methoxy,

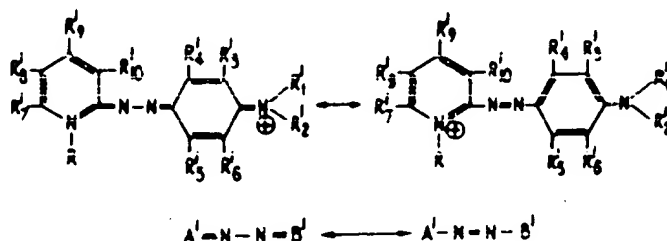
R'_5 and/or R'_6 represents a hydrogen atom, a halogen atom, preferably chlorine, an alkyl group having 1 to 4 carbon atoms, preferably methyl, or a nitro, amino or acetylamino group,

or R'_5 and R'_6 together form, with the carbon atoms to which they are attached, a 6-membered unsaturated ring, preferably benzene, carrying a chelating substituent, preferably hydroxyl, with one of the nitrogen atoms of the azo group, in which case R'_1 , R'_2 , R'_3 and R'_4 only represent a hydrogen atom, and

Z^- represents an anion derived from an inorganic or organic acid such as a halide (e.g. iodide, chloride or bromide), fluoborate, perchlorate, sulphate or acetate, in particular methosulphate;

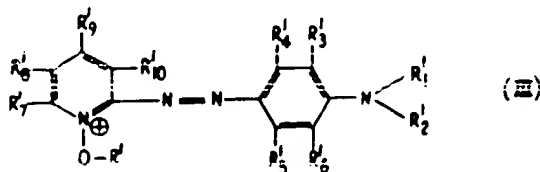
or a mesomeric form thereof, makes it possible to obtain compositions which have improved dyeing properties because of the greater solubility of these compounds. Compared to the known dyestuffs and, amongst others those described in British Patent Specification No. 1,360,562, those of formula (II) offer the advantage of greater solubility in the solvents usually employed in cosmetics such as water, the alcohols and mixtures thereof.

These compounds are quaternary azo dyestuffs which can be represented by the two mesomeric forms



The dyestuffs of the general formula (II) give dyeing compositions which have an increased affinity to keratin fibres and in particular to human hair. Furthermore, the dyeings produced with the aid of this type of dyestuff have improved fastness to light.

The compounds of the general formula (II) are new or known compounds which can be prepared in accordance with a known process which employs compounds of the formula



in which R' represents a lower alkyl radical (i.e. containing 1 to 4 carbon atoms), as described in British Patent Specification No. 1,397,500.

Amongst the known compounds, there may be mentioned the 4'-dialkylamino-benzene-1':2-azo-1-alkyl-pyridinium salts, the pyridinium ring of which is unsubstituted in the 3- and 4-position but can optionally carry a methyl group in the 5- and 6-position, in particular the methosulphate salts of these compounds.

Other particularly valuable known compounds are 4'-dialkylaminobenzene-1':2-azo-1-alkyl-pyridinium salts, the pyridinium ring of which is substituted in the 3- and/or 4-position and optionally in the 5- and/or 6-position by a methyl group, or a chlorine atom in the 5-position. Amongst these compounds there may also be mentioned the compounds substituted in the 5-position by a chlorine atom, wherein the 3- and 4-position in the pyridinium ring is not substituted.

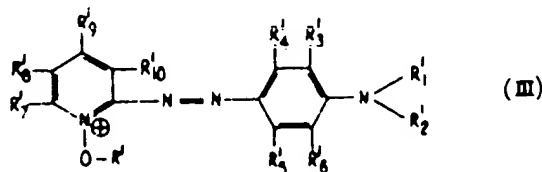
The benzene ring of the abovementioned compounds may of course be substituted in the 2'-position by a chlorine atom or a methyl, nitro, amino or acetylamino group and in the 5'-position by a methyl or methoxy group.

The amino group in the 4'-position can be substituted by alkyl groups such as methyl or ethyl or by hydroxyalkyl groups such as β -hydroxyethyl.

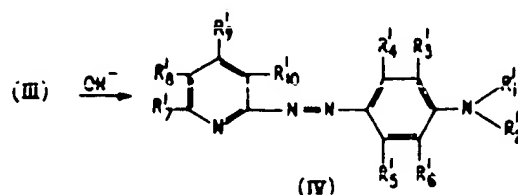
The compounds of the general formula (II) in which R'_{10} , R'_1 , R'_2 , R'_3 , R'_4 , R'_5 , R'_6 , R'_7 , R'_8 , R'_9 , R and Z^- are as defined above, with the proviso that at least one of R'_5 and R'_6 represents a cyano group, are considered to be novel.

Other novel compounds of the general formula (II) are those in which R', and R', do not represent a cyano group and R', and R', together with the carbon atoms to which they are attached form a 6-membered unsaturated ring carrying a hydroxyl substituent chelated with a nitrogen atom of the azo group, in which case R',, R',, R', and R', denote hydrogen, with R',, R',, R and Z- having the same meanings as indicated above and also R', and R',, subject to the above proviso.

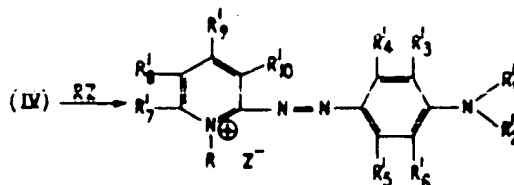
The compounds of the general formula (II) can be prepared from compounds of the formula



in which R' is as hereinbefore defined, as described in British Patent Specification No. 1,397,500. These compounds are subjected to the action of alkali so as to give a compound of formula (IV), in accordance with the well-known reaction



the compounds of formula (IV) finally being treated with an alkylating agent RZ, wherein R and Z are as defined above, so as to give the compounds of the general formula II in accordance with the reaction



wherein R', R', R', R', R', R', R', R', R', R', Z and R are as defined above.

The present invention provides compositions suitable for dyeing keratin fibres, in particular human hair, which are in the form of solutions. The compositions according to the invention are aqueous or aqueous-alcoholic solutions which are easily prepared by dissolving one or more compounds of formula (II) in water or in a mixture of water and alcohol.

The concentration of the dyestuffs of formula (II) in the dyeing compositions according to this invention can vary within wide limits because of the high affinity of these compounds for the keratin fibres. This concentration is generally from 0.0005 to 5% by weight, preferably from 0.01 to 1.5%.

The pH of the said compositions is generally from 3 to 12, especially from 3 to 8. It can be adjusted to the desired value by adding an acid such as *ortho*-phosphoric acid, citric acid or acetic acid or a base such as triethanolamine, monoethanolamine or ammonia.

The compositions according to the present invention may contain, as the sole dyestuff, the dyestuffs of formula (II) in which case they make it possible to obtain, on the hair, shades which are rich in reflection and range from orange to blue. However, these compositions may contain other direct dyestuffs such as azo, anthraquinone or nitrobenzene dyestuffs, or indoanilines indophenols or indamines.

They can also contain various adjuvants usually employed in such compositions, for example anionic, cationic, non-ionic, amphoteric or zwitter-ionic surface-active agents, oxidising agents, synergistic agents or foam stabilisers, sequestering agents, super-fating agents, thickeners, preservatives, dispersing agents, swelling agents, penetrating agents, emollients and perfumes. They can furthermore be packaged in aerosol containers.

Dyeing of human hair by means of the dyeing compositions according to this invention can be carried out in the usual manner by applying the composition to the

hair, with which it is left in contact for a period varying from, for example, 3 to 30 minutes; this application is followed by rinsing and, if appropriate, washing and drying the hair.

The present invention also provides hair wave-setting lotions which are in the form of an aqueous-alcoholic solution containing at least one resin conventionally used in such compositions and at least one compound of formula (II).

The wavesetting lotions according to the invention in general contain from 20 to 70% by weight of a low molecular weight alcohol (i.e. of 1 to 6 carbon atoms) and from 1 to 3% by weight of resin.

Amongst the resins which may be present in the wavesetting lotions, there may be mentioned film-forming polymers such as polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, copolymers of vinyl acetate and an unsaturated carboxylic acid such as crotonic acid, copolymers resulting from the copolymerisation of vinyl acetate, crotonic acid and an acrylate or methacrylate ester, copolymers resulting from the copolymerisation of vinyl acetate and an alkyl vinyl ether, copolymers resulting from the copolymerisation of vinyl acetate, crotonic acid and a vinyl ester of an acid having a long (i.e. of at least 8 carbon atoms) hydrocarbon chain, or an allyl or methallyl ester of an acid having a long hydrocarbon chain, copolymers resulting from the copolymerisation of an ester derived from an unsaturated alcohol and an acid having a short (i.e. of less than 8 carbon atoms) hydrocarbon chain, an unsaturated short-chain acid and at least one ester derived from a short chain saturated alcohol and an unsaturated acid, and copolymers resulting from the copolymerisation of at least one unsaturated ester and at least one unsaturated acid.

Amongst the preferred resins there may be mentioned polyvinylpyrrolidone having a molecular weight of 10,000 to 70,000, copolymers of 10% of crotonic acid and 90% of vinyl acetate, having a molecular weight of 10,000 to 70,000, copolymers of vinylpyrrolidone (PVP) and vinyl acetate (VA) having a molecular weight of 30,000 to 200,000, the PVP:VA ratio being from 30:70 to 70:30, copolymers of maleic anhydride and methyl vinyl ether in a molar ratio of, preferably, 1:1, having a specific viscosity of from 0.1 to 3.5 when measured at 25°C at a concentration of 1 g in 100 cm³ of methyl ethyl ketone, the monoethyl esters, monoisopropyl esters or monobutyl esters of a copolymer of maleic anhydride and methyl vinyl ether, a copolymer of maleic anhydride with butyl vinyl ether, the molar ratio of maleic anhydride to butyl vinyl ether being 1:1, terpolymers of methyl methacrylate (15—25%), stearyl methacrylate (18—28%) and dimethylaminoethyl methacrylate (52—62%) quaternised with dimethylsulphate, and terpolymers of vinyl acetate (75—85%), allyl stearate (10—20%) and allyloxyacetic acid (3—10%).

The low molecular weight alcohols which are used for producing the wavesetting lotions according to this invention are preferably ethanol and isopropanol.

The wavesetting lotions according to the invention can contain dyestuffs of formula (II) as the sole dyestuff, in which case they constitute what are conventionally called tinting compositions. However, they can also contain other direct dyestuffs, such as those mentioned above. They can furthermore also contain adjuvants such as those mentioned above.

The wavesetting lotions according to the invention can be employed in the usual manner by applying them to moist previously washed and rinsed hair and the rolling-up and drying the hair.

The dyestuffs of formula (II) can also be employed in the form of hair lacquers, which contain at least one cosmetic resin and at least one compound of the formula (II) in an alcoholic solution. The alcohols used in these lacquers are low molecular weight alcohols such as ethanol or isopropanol.

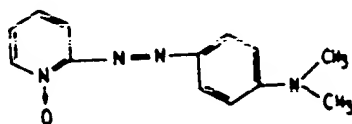
The cosmetic resins employed can be those mentioned above.

The following Examples 1 to 17 illustrate the preparation of compounds used in the compositions of the present invention, which are illustrated in Examples I to XXV.

EXAMPLE 1

Preparation of 4'-dimethylaminobenzene-1':2-azo-1-methyl-pyridinium methosulphate.

A) Preparation of 4'-dimethylaminobenzene-1':2-azo-pyridine N-oxide of the formula



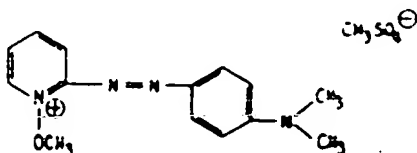
A solution, cooled to 0°C, of 0.1 mol of the N-oxide of pyridine-2-diazonium chloride, prepared according to Katritzky, J.C.S. 1957 p. 191, is added slowly to a solution of 12.1 g of N,N-dimethylaniline in 12 cm³ of acetic acid, whilst keeping the temperature at +5°C.

The mixture is stirred for 30 minutes and twice 40 cm³ of a 40% strength aqueous solution of sodium acetate are added. The precipitate obtained is filtered off, washed with water and dried. After recrystallisation from 50% strength alcohol, a product having a melting point of 188°C is obtained.

Elementary analysis for C₁₃H₁₄N₄O

Calculated:	%	C 64.45	H 5.79	N 23.15
Found:	%	64.25	6.11	22.95

B) Preparation of 4'-dimethylaminobenzene-1':2-azo-1-methoxy-pyridinium methosulphate of the formula



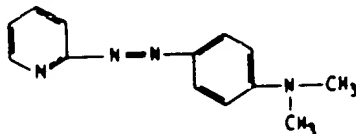
0.1 mol of compound obtained in stage A is suspended in 100 cm³ of N-methylpyrrolidone-2. 35 cm³ of dimethyl sulphate are added dropwise whilst stirring vigorously, and the mixture is stirred for 1 hour. It is filtered and the product is then washed with 35 cm³ of acetone and recrystallised from alcohol.

The product obtained has a melting point of 197°C.

Elementary analysis: C₁₃H₂₀N₄O₆S

Calculated:	%	C 48.90	H 5.43	N 15.22
Found:	%	49.08	5.62	15.10

C) Preparation of 4'-dimethylaminobenzene-1':2-azo-pyridine of the formula

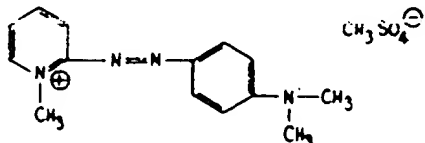


0.1 mol of the compound obtained in stage B is dissolved in 600 cm³ of 90% strength alcohol and 42 cm³ of concentrated ammonia. The mixture is heated under reflux for 1 hour and the solvent is then distilled off under reduced pressure. The residue is taken up in 100 cm³ of water and filtered off. After recrystallisation from cyclohexane, a product having a melting point of 112°C is obtained.

Elementary analysis for C₁₃H₁₄N₄O

Calculated:	%	C 69.00	H 6.2	N 24.8
Found:	%	69.03	5.93	25.06

D) Preparation of 4'-dimethylaminobenzene-1':2-azo-1-methyl-pyridinium methosulphate of the formula



0.1 mol of the compound obtained in stage C is dissolved in 100 cm³ of N-methylpyrrolidone-2. 19.5 cm³ of dimethyl sulphate are added dropwise whilst stirring vigorously. The mixture is stirred for 1 hour and is then filtered, and the product is washed with 35 cm³ of acetone and recrystallised from alcohol.

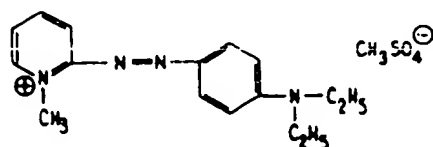
The product obtained has a melting point of 210°C.

Elementary analysis: C₁₃H₂₀N₄O₆S

Calculated:	%	C 51.12	H 5.68	N 15.95
Found:	%	51.12	5.77	16.04

EXAMPLE 2

Preparation of 4' - diethylaminobenzene - 1':2 - azo - 1 - methyl - pyridinium methosulphate of the formula:



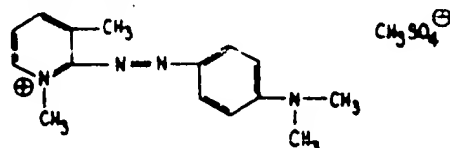
This compound is obtained in accordance with the method described in Example 1, with the sole difference that a solution of N,N-diethylaniline is used in stage A. The resulting product has a melting point of 129°C.

Elementary analysis: $C_{11}H_{16}N_4O_4S$

Calculated:	%	C 53.70	H 6.32	N 14.73
Found:	%	53.34	6.49	14.72

EXAMPLE 3

Preparation of 4' - dimethylaminobenzene - 1':2 - azo - 1,3 - dimethyl - pyridinium methosulphate of the formula:



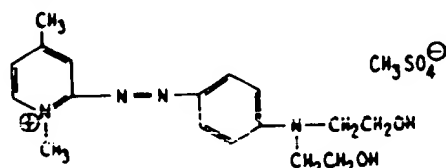
This compound is obtained in accordance with the method described in Example 1, with the sole difference that the diazotised amine is 2-amino-3-methyl-pyridine oxide. The melting point of the resulting product is 210°C.

Elementary analysis $S_{16}H_{22}N_4O_4S$

Calculated:	%	C 52.44	H 6.01	N 15.30
Found:	%	52.47	6.16	15.11

EXAMPLE 4

Preparation of 4' - bis(β - hydroxyethyl)aminobenzene - 1':2 - azo - 1,4 - dimethylpyridinium methosulphate of the formula



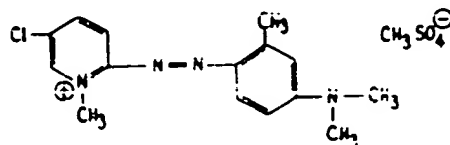
This compound is obtained in accordance with the method described in Example 1, with the sole difference that the diazonium salt used in stage A is derived from 2-amino-4-methyl-pyridine N-oxide and that the aniline derivative used is N,N-(β -hydroxyethyl)aniline. After recrystallisation from alcohol, a product having a melting point of 165°C is obtained.

Elementary analysis: $C_{18}H_{26}N_4O_6S$

Calculated:	%	C 50.70	H 6.10	N 13.13
Found:	%	50.73	6.11	13.27

EXAMPLE 5

Preparation of 4' - dimethylamino - 2' - methylbenzene - 1':2 - azo - 5 - chloro - 1 - methyl - pyridinium methosulphate of the formula:

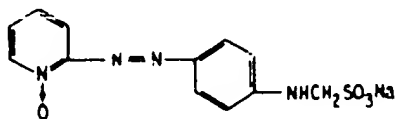


This compound is obtained in accordance with the method described in Example 1, with the sole difference that in stage A N-oxy-5-chloropyridine-2-diazonium chloride and 3-methyl-N,N-dimethylaniline are used. The product melts at 242°C.

EXAMPLE 6

Preparation of 4'-aminobenzene-1':2-azo-1-methylpyridinium methosulphate.

- A) Preparation of the sodium salt of 1'-oxy-pyridine-2'-(4-azo-anilinomethylsulphonic acid) of the formula:

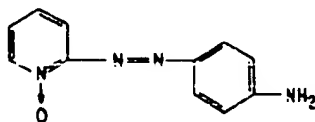


0.11 mol of aniline N-methyl ω -sodium sulphonate are dissolved in 17 cm³ of water. 53 g of crystalline sodium acetate are added and the mixture is cooled to +5°C. A cold solution of 0.1 mol of N-oxypyridine-2-diazonium chloride prepared according to Katritzky, J.C.S. 1957 p. 191 is added slowly. Thereafter 130 g of crystalline sodium acetate are added and the mixture is allowed to react for 1 hour. The product is filtered off and dried over phosphorus pentoxide. After recrystallisation from water, the product has a melting point of 160°C.

Elementary analysis C₁₂H₁₁N₄O₄Na.3H₂O

Calculated:	%	C 37.50	H 4.32	N 14.55
Found:	%	37.99	3.46	14.26

- B) Preparation of 4'-aminobenzene-1':2-azo-pyridine N-oxide of the formula:

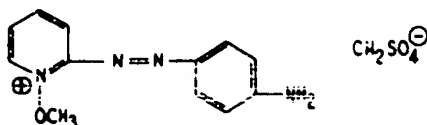


0.1 mol of the compound obtained in stage A is dissolved in 200 cm³ of 10% strength ammonia and the mixture is heated to 60°C for 5 hours. It is allowed to cool and then filtered, and the product is washed with water and dried. After recrystallisation from methanol, the product has a melting point of 300°C (with decomposition).

Elementary analysis: C₁₁H₁₀N₄O

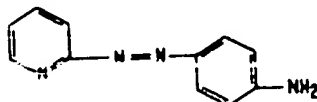
Calculated:	%	C 61.70	H 4.67	N 26.17
Found:	%	61.79	4.93	25.99

- C) Preparation of 4'-aminobenzene-1':2-azo-1-methoxypyridinium methosulphate of the formula:



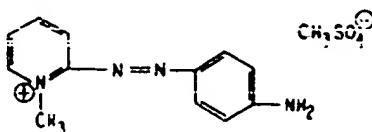
0.1 mol of compound obtained in stage B is dissolved in 100 cm³ of N-methylpyrrolidone-2. 12.5 cm³ of dimethyl sulphate are added dropwise and the reactants are left in contact overnight. The dyestuff is precipitated by adding ethyl acetate. It is filtered off, washed with alcohol and then with ether, and dried.

- D) Preparation of 4'-aminobenzene-1':2-azo-pyridine of the formula



0.1 mol of the compound obtained in stage C is dissolved in 600 cm³ of 90% strength alcohol and 42 cm³ of concentrated ammonia and the mixture is heated under reflux for 1 hour. The solvent is distilled under reduced pressure and the product is recrystallised from ethyl acetate.

- E) Preparation of 4'-aminobenzene-1':2-azo-1-methylpyridinium methosulphate of the formula:



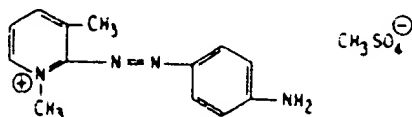
0.1 mol of the compound obtained in stage D is dissolved in 100 cm³ of N-methylpyrrolidone-2. 12.5 cm³ of dimethyl sulphate are added whilst stirring and the mixture is allowed to react for 1 hour 30 minutes. 400 cm³ of ethyl acetate are added and the oil obtained is decanted and crystallised from absolute alcohol. The product has a melting point of 193°C.

Elementary analysis for: C₁₃H₁₄N₂O₂S

Calculated:	%	C 48.15	H 4.94	N 17.29
Found:	%	48.28	5.00	17.21

EXAMPLE 7

Preparation of 4' - aminobenzene - 1':2 - azo - 1,3 - dimethyl - pyridinium methosulphate of the formula:



This compound is obtained in accordance with the method described in Example 6, the amine diazotised being 2-amino-3-methyl-pyridine N-oxide. After recrystallisation from absolute alcohol, the product has a melting point of 183°C.

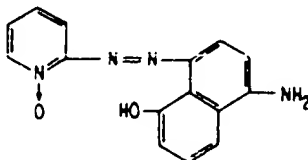
Elementary analysis: C₁₄H₁₁N₃O₂S

Calculated:	%	C 49.70	H 5.33	N 16.56
Found:	%	49.54	5.35	16.35

EXAMPLE 8

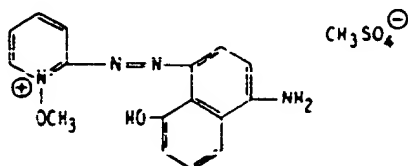
Preparation of 4' - amino - 8' - hydroxy - naphthalene - 1':2 - azo - 1 - methyl-pyridinium methosulphate.

A) Preparation of 4' - amino - 8' - hydroxy - naphthalene - 1':2 - azo - pyridine N-oxide of the formula:



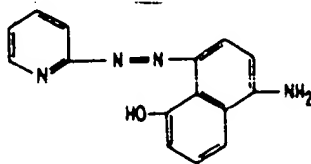
A solution, cooled to 0°C, of 0.1 mol of N-oxypyridine-2-diazonium chloride prepared according to Katritzky, J.C.S. 1957 p. 191, is added to a solution of 5-acetoxy-1-naphthylamine hydrochloride in 900 cm³ of 80% strength acetic acid whilst keeping the temperature at +5°C. The reaction mixture is brought to pH 4 by adding sodium acetate. It is stirred for 30 minutes, 1.5 litres of water are then added and the product is filtered off and dried. The product obtained is dissolved in 450 cm³ of 2-methoxy-ethanol. 150 cm³ of sodium hydroxide solution are added and the mixture is stirred for 30 minutes. It is then poured rapidly into 3 litres of water and neutralised with acetic acid, and the product is dried. It has a melting point of 280°C (with decomposition).

B) Preparation of 4' - amino - 8' - hydroxy - naphthalene - 1':2 - azo - 1 - methoxy-pyridinium methosulphate of the formula:



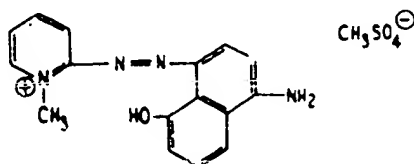
0.1 mol of the compound obtained in stage A is dissolved in 125 cm³ of N-methylpyrrolidone-2 and 15 cm³ of dimethyl sulphate are added dropwise whilst stirring. Stirring is continued to the end of the reaction. The product is filtered off after adding ethyl acetate to the reaction mixture.

- C) Preparation of 4' - amino - 8' - hydroxy - naphthalene - 1':2 - azo - pyridine of the formula:



0.1 mol of the compound obtained in stage B is dissolved in 1 litre of 90% strength alcohol and 100 cm³ of concentrated ammonia. The mixture is heated under reflux for 1 hour and evaporated to dryness. The product is worked into a paste with water, filtered off and dried.

- D) Preparation of 4' - amino - 8' - hydroxy - naphthalene - 1':2 - azo - 1 - methyl - pyridinium methosulphate of the formula:

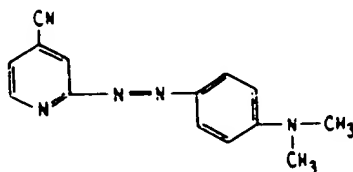


0.1 mol of the compound obtained in stage C is dissolved in 125 cm³ of N-methylpyrrolidone-2. 15 cm³ of dimethyl sulphate are added dropwise whilst stirring and the mixture is stirred until the reaction is complete. The product is precipitated by adding ethyl acetate. It has a melting point of 250°C (with decomposition).

EXAMPLE 9

Preparation of 4' - dimethylaminobenzene - 1':2 - azo - 4 - cyano - 1 - methyl - pyridinium methosulphate.

- A) Preparation of 4' - dimethylaminobenzene - 1':2 - azo - 4 - cyano - pyridine of the formula:

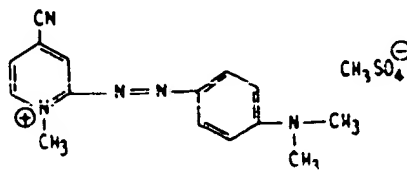


0.1 mol of the compound obtained in Example 1, stage B, is dissolved in 40 cm³ of water and 10 g of sodium cyanide in 50 cm³ of water are added dropwise whilst stirring. The mixture is heated to 80°C for 3 hours and is then allowed to cool, and is filtered. After recrystallisation from chloroform, the product has a melting point of 190°C.

Elementary analysis: C₁₁H₁₁N₃

Calculated:	%	C 66.95	H 5.18	N 27.87
Found:	%	66.81	5.18	27.78

- B) Preparation of 4' - dimethylaminobenzene - 1':2 - azo - 4 - cyano - 1 - methyl - pyridinium methosulphate of the formula:

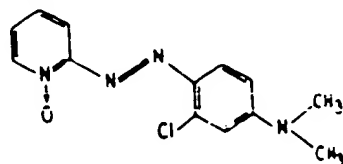


0.1 mol of the compound in stage A is dissolved in 300 cm³ of N-methylpyrrolidone-2 and 15 cm³ of dimethyl sulphate are added dropwise. The mixture is heated to 50°C until reaction is complete. The product is precipitated by adding ethyl acetate and is purified by chromatography on a silica gel column. The product has a melting point of 208°C.

EXAMPLE 10

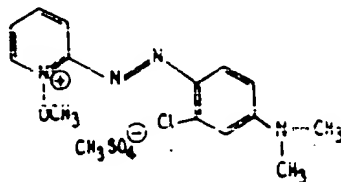
Preparation of 2'-chloro-4'-dimethylaminobenzene-1':2-azo-1-methyl-pyridinium methosulphate.

A) Preparation of 2'-chloro-4'-dimethylaminobenzene-1':2-azo-pyridine N-oxide of the formula:



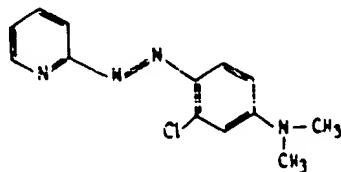
5 g (0.032 mol) of meta-chloro-N,N-dimethylaniline are dissolved in 6 cm³ of acetic acid and the solution is cooled to 5°C. A solution of the diazonium salt obtained according to Example 1, starting from 0.032 mol of 2-aminopyridine N-oxide, is now added slowly. The precipitate obtained is suspended in water and a saturated sodium bicarbonate solution is added until the mixture is neutral. The product is filtered off and dried, and the dyestuff obtained is crystallised from ethyl alcohol. It melts at 202°C.

B) Preparation of 2'-chloro-4'-dimethylaminobenzene-1':2-azo-1-methoxy-pyridinium methosulphate:



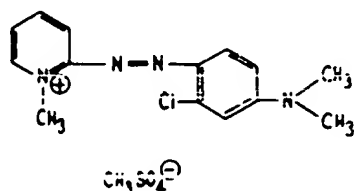
4.45 g of the compound obtained in stage A are dissolved in 11.15 cm³ of N-methylpyrrolidone and 1.70 cm³ of dimethyl sulphate are added dropwise whilst stirring. Stirring is continued for 1 hour and the precipitate formed is filtered off and washed with acetone.

C) Preparation of 2'-chloro-4'-dimethylaminobenzene-1':2-azo-pyridine:



5 cm³ of concentrated ammonia are added to a solution of 4.75 g of the compound obtained in stage B, in 73 cm³ of 90% strength ethanol. Thereafter the mixture is heated under reflux until the reaction has finished. The solution is then concentrated to dryness under reduced pressure and the reaction product is purified by chromatography on a silica gel column, using ethyl acetate as the eluant.

D) Preparation of 2'-chloro-4'-dimethylaminobenzene-1':2-azo-1-methyl-pyridinium methosulphate:



3 g of the compound obtained in stage C are dissolved in 7 cm³ of N-methylpyrrolidone and the mixture is stirred vigorously while slowly adding 1.2 cm³ of dimethyl sulphate. Stirring is continued for 1 hour after the end of the addition and the precipitate obtained is filtered off; it is then washed with ethyl acetate and dried.

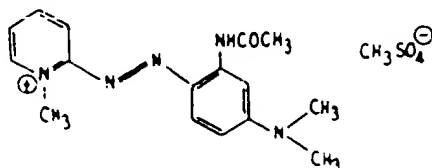
The dyestuff is purified by crystallisation from methanol. It melts at 225°C.

Analysis $C_{15}H_{17}N_3O_4S\ Cl$

Calculated	%	N 14.48
Found:	%	14.72—14.41

EXAMPLE 11

Preparation of 2' - acetyl amino - 4' - dimethylaminobenzene - 1':2 - azo - 1 - methyl - pyridinium methosulphate of the formula:



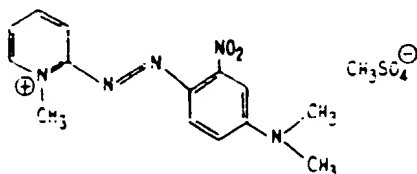
This compound is obtained in accordance with the method described in Example 1, with the sole difference that in stage A a solution of meta-acetyl amino-N,N-dimethylaniline is used. The resulting product melts at 225°C after recrystallisation from methanol.

Elementary analysis: $C_{17}H_{21}N_3O_4S$

Calculated	%	C 49.89	H 5.62	N 17.11
Found:	%	49.66	5.45	17.31

EXAMPLE 12

Preparation of 2' - nitro - 4' - dimethylaminobenzene - 1':2 - azo - 1 - methyl - pyridinium methosulphate of the formula



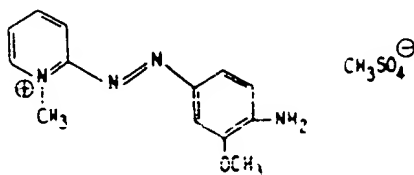
This compound is prepared in accordance with the method described in Example 1, with the sole difference that in stage A a solution of meta-nitro-N,N-dimethylaniline is used. The product obtained melts at 254°C after recrystallisation from methanol.

Elementary analysis: $C_{17}H_{19}N_3O_6S \cdot \frac{1}{2}CH_3OH$

Calculated:	%	C 45.00	H 5.08	N 16.94
Found:	%	44.81	5.33	17.08

EXAMPLE 13

Preparation of 4' - amino - 3' - methoxybenzene - 1':2 - azo - 1 - methyl - pyridinium methosulphate of the formula:



This compound is obtained in accordance with the method described in Example 1, with the sole difference that in stage A a solution of ortho-anisidine is used. The melting point of the resulting product is 205°C after recrystallisation from alcohol.

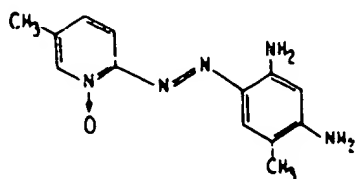
Elementary analysis: $C_{17}H_{19}N_3O_4S$

Calculated	%	C 47.50	H 5.08	N 15.82
Found:	%	47.28	5.28	15.72

EXAMPLE 14

Preparation of 2',4' - diamino - 5' - methylbenzene - 1':2 - azo - 1,5 - dimethyl - pyridinium methosulphate.

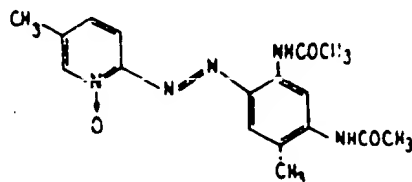
A) Preparation of 2',4' - diamino - 5' - methylbenzene - 1':2 - azo - 5 - methyl - pyridine N-oxide of the formula



A solution, cooled to 0°C, of 0.1 mol of 5-methyl-N-oxy-pyridine-2-diazonium chloride prepared according to Katritzky, J. Chem. Soc. 1957, page 191, is added slowly, whilst maintaining the temperature at +5°C, to a solution of 12.2 g of 2,4-diaminotoluene in 20 cm³ of acetic acid.

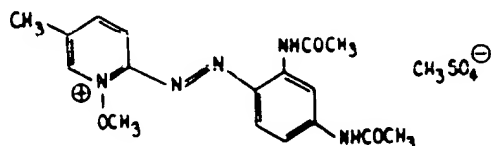
The mixture is stirred for 30 minutes and 34 g of crystalline sodium acetate is then added. The precipitate obtained is filtered off, washed with water and dried.

B) Preparation of 2',4' - diacetyl-amino - 5' - methylbenzene - 1':2 - azo - 5 - methyl - pyridine N-oxide of the formula



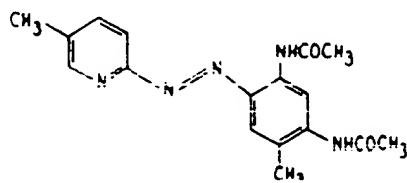
0.1 mol of the compound obtained in stage A is dissolved in 300 cm³ of acetic acid, 88 g of acetic anhydride are added dropwise and the mixture is heated for 2 hours on a boiling water bath. The reaction mixture is then allowed to cool and is poured onto 500 g of ice. The solution thus obtained is neutralised with sodium carbonate. The precipitate obtained is filtered off, washed with water and dried.

C) Preparation of 2',4' - diacetyl-amino - 5' - methylbenzene - 1':2 - azo - 1 - methoxy - 5 - methyl - pyridinium methylsulphate of the formula:



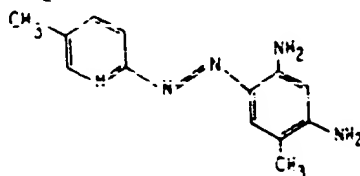
0.1 mol of the compound obtained in stage B is dissolved in 160 cm³ of N-methylpyrrolidone-2. 9 cm³ of dimethyl sulphate are added dropwise while stirring vigorously. The reactants are left in contact overnight and a further 2 cm³ of dimethyl sulphate are then added. The precipitate obtained is filtered off, washed with acetone and dried.

D) Preparation of 2',4' - diacetyl-amino - 5' - methylbenzene - 1':2 - azo - 5 - methyl - pyridine of the formula



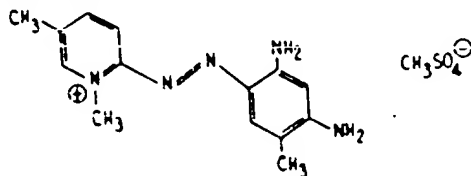
0.1 mol of the compound obtained in stage C is dissolved in 2,300 cm³ of 90% strength alcohol. 190 cm³ of concentrated ammonia are added and the mixture is stirred for 45 minutes at ambient temperature. The solvent is distilled under reduced pressure. The residue is taken up in 100 cm³ of water, filtered off and dried.

E) Preparation of 2',4' - diamino - 5' - methylbenzene - 1':2 - azo - 5 - methyl - pyridine of the formula



0.1 mol of compound obtained in stage D is dissolved in 100 cm³ of 5 N hydrochloric acid and the reaction mixture is heated under reflux for 3 hours. It is then cooled and neutralised by adding sodium bicarbonate. It is extracted with chloroform and the solvent is then distilled under reduced pressure. The product is purified by chromatography on silica gel, using dichloroethane as the eluant.

F) Preparation of 2',4' - diamino - 5' - methylbenzene - 1':2 - azo - 1,5 - dimethylpyridinium methosulphate of the formula



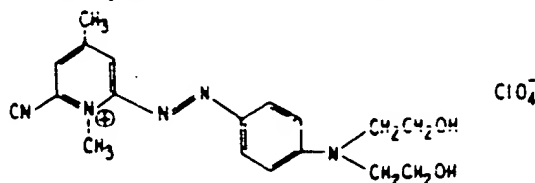
0.1 mol of the compound obtained in stage E is dissolved in 7,500 cm³ of dichloroethane. 10 cm³ of dimethyl sulphate are added dropwise and the mixture is stirred for 30 minutes. It is then filtered and the product obtained is recrystallised from alcohol. It melts at 252°C.

Elementary analysis: C₁₃H₂₁N₃O₄S

Calculated:	%	C 49.08	H 5.72	N 19.04
Found:	%	48.78	5.88	19.28

EXAMPLE 15

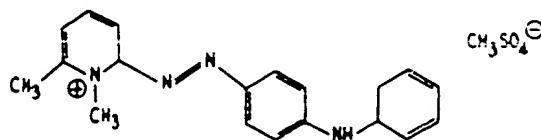
Preparation of 4' - bis(β - hydroxyethyl)aminobenzene - 1':2 - azo - 6 - cyano - 1,4 - dimethyl - pyridinium perchlorate of the formula



This compound is obtained according to the method described in Example 9, with the sole difference that in stage A a solution of 4'-bis(β-hydroxyethyl)aminobenzene-1':2-azo-1-methoxy-4-methyl-pyridinium methosulphate is used. The product is converted to the perchlorate salt by dissolving it in water and adding an aqueous solution of sodium perchlorate. It melts at 210°C, with decomposition.

EXAMPLE 16

Preparation of 4' - phenylaminobenzene - 1':2 - azo - 1,6 - dimethyl - pyridinium methosulphate of the formula



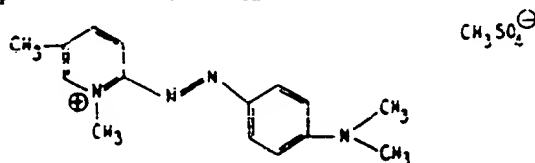
This compound is obtained in accordance with the method described in Example 1, with the sole difference that in stage A 6-methyl-N-oxy-pyridine-2-diazonium chloride and diphenylamine are used. After recrystallisation from methanol, the product melts at 220°C—222°C.

Elementary analysis: C₁₇H₂₃N₃O₃S

Calculated:	%	C 49.89	H 5.62	N 17.11
Found:	%	49.66	5.45	17.31

EXAMPLE 17

Preparation of 4' - dimethylaminobenzene - 1':2 - azo - 1,5 - dimethyl - pyridinium methosulphate of the formula



This compound is obtained in accordance with the method described in Example 1, with the sole difference that in stage A 5-methyl-N-oxy-pyridine-2-diazonium chloride and the same N,N-dimethylaniline are used.

After recrystallisation from ethanol, the product melts at 168°C.

Elementary analysis: $C_{16}H_{22}N_4O_4S$

Calculated	%	C 52.48	H 6.01	N 15.30
Found:	%	52.18	6.07	15.22

These compounds prepared in accordance with conventional methods, can also be used in the compositions now described.

EXAMPLES OF COMPOSITIONS

EXAMPLE I

The following dyeing composition is prepared:

2'-Acetylamino-4'-dimethylaminobenzene-1': 2-azo-1-methylpyridinium methosulphate	0.02 g	
2-Amino-4-hydroxybenzene-1': 1'-azo-4'-hydroxybenzene	0.02 g	
Quaternised copolymer of vinylpyrrolidone and a lower dialkylaminoalkyl acrylate, of molecular weight about 1,000,000 (sold under the Registered Trade Mark "Gafquat" 755)		
Water, q.s.	100 g	

This composition is applied for 5 minutes to naturally grey hair comprising 95% of white hair, which has been shampooed beforehand.

A rose-grey shade is obtained.

EXAMPLE II

The following composition is prepared:

4'-Phenylaminobenzene-1': 2-azo-1,6-dimethylpyridinium methosulphate	0.01 g	
(1-Anthraquinonylaminoethyl)-trimethylammonium methosulphate	0.03 g	
Quaternised cellulose sold under the name of JR 400 (a cellulose ether having a backbone of anhydroglucose units with pendant groups containing quaternary nitrogen atoms)	2 g	
Triethanolamine, q.s. pH 8		
Water, q.s.	100 g	

This slightly gelled composition is applied to hair which has beforehand been washed and bleached, and is left thereon for 10 minutes. A pearlescent intense rose sheet is obtained.

EXAMPLE III

The following composition is prepared:

4'-Amino-8'-hydroxynaphthalene-1': 2-azo-1-methylpyridinium methosulphate	0.03 g	
4'-Bis(β-hydroxyethyl)aminobenzene-1': 2-azo-1,4-dimethylpyridinium methosulphate	0.02 g	
A copolymer of vinyl acetate and crotonic acid (90/10)	2 g	
2-Amino-2-methyl-1-propanol, q.s.p.	100%	
Ethyl alcohol, q.s.p.	100 cc	

This alcoholic solution is packaged as an aerosol with a mixture of F.11 and F.12, F.11 being trichlorofluoromethane and F.12 being dichlorodifluoromethane, in the ratio of 60:40, using 30 g of solution and 70 g of propellant.

When applied to hair which has been dyed chestnut-coloured, this lacquer imparts an attractive ashen sheen to the head of hair.

EXAMPLE IV

The following solution is prepared:

	4'-Dimethylaminobenzene-1': 2-azo-1-methylpyridinium methosulphate	0.010 g	
5	A copolymer of vinyl acetate and crotonic acid (90/10)	2 g	5
	2-Amino-2-methyl-1-propanol, q.s.	100%	
	Ethyl alcohol, q.s.p.	100 cc	

This alcoholic solution is packaged as an aerosol with a mixture of F.11 and F.12, F.11, being trichlorofluoromethane and F.12 being dichlorodifluoromethane, in the ratio of 60:40, using 30 g of solution and 70 g of propellant.

When applied to hair which has been dyed light chestnut-coloured, this lacquer imparts a violet sheen to the head of hair.

EXAMPLE V

The following solution is prepared:

15	Dyestuff of Example 10	0.050 g	15
	A copolymer of vinyl acetate and crotonic acid (90/10)	1.8 g	
	A copolymer of vinyl acetate and vinylpyrrolidone (40/60)	0.3 g	
	Ethyl alcohol, q.s.p. 50°		
	Triethanolamine, q.s. pH 7		
20	Water q.s.p.	100 cc	20

When applied to hair dyed chestnut, this wave-setting lotion imparts a very luminous violet sheen to the head of hair.

EXAMPLE VI

The following composition is prepared:

25	2'-Nitro-4'-dimethylaminobenzene-1': 2-azo-1-methylpyridinium methosulphate	0.5 g	25
	Ethanol	40 g	
	A copolymer of vinylpyrrolidone and vinyl acetate (30/70)	1.5 g	
30	Double chloride of zinc and N-[4'-(N-ethyl-N'-acetylaminioethyl)-aminophenyl]-2-aza-3-amino-benzoquinonediimine	0.1 g	30
	Triethanolamine, q.s. pH 7		
	Water q.s.	100 g	

This composition is applied as a wavesetting lotion to naturally grey hair comprising 95% of white hair. A cardinal-violet tint is obtained.

EXAMPLE VII

The following composition is prepared:

35	4'-Amino-3'-methoxybenzene-1': 2-azo-1-methylpyridinium methosulphate	0.02 g	35
	Ethanol	50 g	
40	Monobutyl ester of a copolymer of methyl vinyl ether and maleic anhydride (sold under the Registered Trade Mark "Gantrez" ES 425)	2 g	40
	1,4-(β-Morpholinoethyl)diamino-anthraquinone	0.2 g	
	Triethanolamine q.s. pH 8		
45	Water q.s.	100 g	45

This composition is applied to bleached hair as a wavesetting lotion. A mauve shade is obtained.

EXAMPLE VIII

The following composition is prepared:

50	2',4'-Diamino-5'-methyl-benzene-1': 2-azo-1,5-dimethylpyridinium methosulphate	0.04 g	50
	Ethanol	70 g	
	Polyvinylpyrrolidone K/30	3 g	

Methyl [(1-anthraquinonylamino-propyl)-trimethylammonium] sulphate	0.5 g	
Triethanolamine q.s. pH 6.5		
Water q.s.	100 g	

5 When this composition is applied as a wavesetting lotion to naturally 95% white hair, it imparts a salmon rose tint thereto. 5

EXAMPLE IX

The following composition is prepared:

4'-Dimethylamino-benzene-1':2-azo-1,5-dimethyl-pyridinium methosulphate	0.3 g	10
Ethanol	60 g	
A 30/70 copolymer of polyvinylpyrrolidone and vinyl acetate	2.5 g	
2-Amino-4-hydroxy-benzene-1:1'-azo-4'-hydroxybenzene	0.4 g	
Triethanolamine q.s. pH 6		
Water q.s.	100 g	15

When this composition is applied to grey hair as a wavesetting lotion, it imparts a pearlescent copper shade thereto.

EXAMPLE X

The following dyeing composition is prepared:

Dyestuff of Example 1	0.050 g	20
A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	
Ethyl alcohol q.s.p. 50°		
Triethanolamine q.s.p. pH 9		
water q.s.p.	100 cc	25

When applied to natural chestnut hair, this wavesetting lotion imparts an attractive very luminous violet sheen to the head of hair.

EXAMPLE XI

The following dyeing composition is prepared:

Dyestuff of Example 2	0.050 g	30
A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	
Ethyl alcohol q.s.p. 50°		
Triethanolamine q.s.p. pH 7		
Water q.s.p.	100 cc	35

When applied hair dyed chestnut, this wavesetting lotion imparts a violet-chestnut shade to the head of hair.

EXAMPLE XII

The following dyeing composition is prepared:

Dyestuff of Example 6	0.050 g	40
A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	
Ethyl alcohol q.s.p. 50°		
Citric acid q.s.p. pH 5		
Water q.s.p.	100 cc	45

When applied to natural deep chestnut hair, this wavesetting lotion imparts a particularly attractive mahogany sheen to the head of hair.

EXAMPLE XIII

The following dyeing composition is prepared:

	Dyestuff of Example 8	0.050 g	
	90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
5	40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	5
	Ethyl alcohol q.s.p. 50°		
	Citric acid q.s.p. pH 5		
	Water q.s.p.	100 cc	

10 When applied to hair dyed deep blonde, this wavesetting lotion imparts a particularly attractive ashen sheen to the head of hair. 10

EXAMPLE XIV

The following dyeing composition is prepared:

	Dyestuff of Example 3	0.050 g	
	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
15	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	15
	Ethyl alcohol q.s.p. 50°		
	Triethanolamine q.s.p. pH 7		
	Water q.s.p.	100 g	

20 When applied to hair dyed blonde, this wavesetting lotion imparts a particularly luminous rose-blond shade to the head of hair. 20

EXAMPLE XV

The following dyeing composition is prepared:

	Dyestuff of Example 7	0.050 g	
	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
25	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	25
	Ethyl alcohol q.s.p. 50°		
	Citric acid q.s.p. pH 5		
	Water q.s.p.	100 cc	

30 When applied to natural chestnut hair, this wavesetting lotion imparts to the head of hair a splendid orange-red sheen. 30

EXAMPLE XVI

The following dyeing composition is prepared:

	Dyestuff of Example 4	0.050 g	
	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
35	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	35
	Ethyl alcohol q.s.p. 50°		
	Triethanolamine q.s.p. pH 7		
	Water q.s.p.	100 cc	

40 When applied to natural chestnut hair, this wavesetting lotion imparts a very beautiful violine sheen to the head of hair. 40

EXAMPLE XVII

The following dyeing composition is prepared:

	Dyestuff of Example 9	0.050 g	
	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
45	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	45
	Ethyl alcohol q.s.p. 50°		
	Triethanolamine q.s.p. pH 9		
	Water q.s.p.	100 cc	

50 When applied to hair dyed deep chestnut, this wavesetting lotion imparts a splendid iridescent ashen sheen to the head of hair. 50

EXAMPLE XIX

The following dyeing composition is prepared:

	Dyestuff of Example 5	0.050 g	
	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
5	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	5
	Ethyl alcohol q.s.p. 50°		
	Citric acid q.s.p. pH 5		
	Water q.s.p.	100 cc	

When applied to natural deep chestnut hair, this wavesetting lotion imparts a particularly luminous mauve ashen sheen to the head of hair.

EXAMPLE XX

The following dyeing composition is prepared:

	Dyestuff of Example 8	0.0312 g	
	Dyestuff of Example 4	0.0187 g	
15	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	15
	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	
	Ethyl alcohol q.s.p. 50°		
	Triethanolamine q.s.p. pH 7		
	Water q.s.p.	100 cc	

When applied to hair dyed chestnut, this wavesetting lotion imparts an attractive ashen chestnut shade to the head of hair.

EXAMPLE XXI

The following dyeing composition is prepared:

25	Dyestuff of Example 7	0.020 g	
	Dyestuff of Example 9	0.025 g	25
	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	
	Ethyl alcohol q.s.p. 55°		
	Hydrogen peroxide of 200 volumes strength	5 cc	
30	Ortho-phosphoric acid q.s.p. pH 3		30
	Water q.s.p.	100 g	

When applied to natural deep blonde hair, this wavesetting lotion slightly lightens the hair and at the same time imparts a very luminous violine sheen to it.

EXAMPLE XXII

The following dyeing composition is prepared:

35	Dyestuff of Example 4	0.300 g	35
	Hydroxyethylpropylcellulose sold under the Registered Trade Mark "Methocel" 65 Hg by Dow Chemical	0.7 g	
	Monoethanolamine q.s.p. pH 11.4		
	Water q.s.p.	100 g	

When this solution is applied to natural deep chestnut hair and rinsed off after 15 minutes, it imparts a very luminous violine sheet to the head of hair.

EXAMPLE XXIII

The following dyeing composition is prepared:

45	Dyestuff of Example 5	0.400 g	45
	Hydroxyethylpropylcellulose sold under the name of Methocel 65 Hg 4,000 by Dow Chemical	0.7 g	
	Monoethanolamine q.s.p. pH 11.6		
	Water q.s.p.	100 g	

When this solution is applied to natural brown hair and rinsed off after 15 minutes, it imparts a violet sheen to the head of hair.

EXAMPLE XXIV

The following dyeing composition is prepared:

	Dyestuff of Example 7	1.0 g	
	Ethylene glycol monobutyl ether	8 g	
5	Propylene glycol	8 g	5
	Alkylphenol polyethoxy-ether sold under the name of "Remcopal 334", by Messrs. Gerland	22 g	
	Alkylphenol polyethoxy-ether sold under the name of "Remcopal 349" by Messrs. Gerland	22 g	
10	Ammonia, 22° Baumé strength	10 cc	10
	Water q.s.p.	100 g	

20 g of hydrogen peroxide of 20 volumes strength are added to 20 g of the solution thus prepared.

This gives a gel which is applied to chestnut hair. After 30 minutes, the hair is washed. After drying, the head of hair is lightened and has a mahogany chestnut sheen.

EXAMPLE XXV

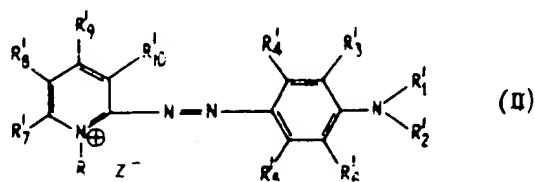
The following dyeing composition is prepared:

	Dyestuff of Example 9	0.035 g	
	Nitro-para-phenylenediamine dyestuff	0.012 g	
20	A 90/10 copolymer of vinyl acetate and crotonic acid	1.8 g	20
	A 40/60 copolymer of vinyl acetate and vinylpyrrolidone	0.3 g	
	Ethyl alcohol q.s.p. 50°		
	Trichanolamine q.s.p. pH 7		
	Water q.s.p.	100 cc	

When applied to natural light chestnut hair, this wavesetting lotion imparts a very luminous violet sheen to the head of hair.

WHAT WE CLAIM IS:—

1. A composition suitable for dyeing human hair which comprises an aqueous or aqueous-alcoholic solution having a pH from 3 to 12 and containing at least one quaternary azo dyestuff of the formula:



in which

- R represents an alkyl group of 1 to 4 carbon atoms;
- R'₁₀ represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms;
- R', represents a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, or a —CN group;
- R', represents a hydrogen or halogen atom or an alkyl group of 1 to 4 carbon atoms;
- R', represents a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, or a cyano group;
- R', represents a hydrogen atom or an alkyl or hydroxyalkyl group of 1 to 4 carbon atoms;
- R', represents a hydrogen atom, an alkyl or hydroxyalkyl group of 1 to 4 carbon atoms or phenyl;
- R', and R', each independently represents a hydrogen atom, or an alkyl or alkoxy group of 1 to 4 carbon atoms;
- R', and R', each independently represents a hydrogen atom, a halogen atom, an alkyl group of 1 to 4 carbon atoms, or a nitro, amino or acetyl amino group, or R', and R', together form, with the carbon atoms at which they are attached, a 6-membered unsaturated ring carrying a substituent which is chelated with one of the nitrogen atoms of the azo group, in which case R',, R',, R', and R', each represent a hydrogen atom and
- Z represents an anion of an inorganic or organic acid; or a mesomeric form thereof.

2. A composition according to claim 1 in which the quaternary azo compound is present in an amount from 0.0005 to 5% by weight.

3. A composition according to claim 1 or 2 which contains a low molecular weight alcohol.

4. A composition according to claim 3 which contains ethanol or isopropanol.

5. A composition according to any one of the preceding claims which contains a further azo, or an anthraquinone or, nitrobenzene dyestuff or an indoaniline, indophenol or indamine.

6. A composition according to any one of the preceding claims in the form of a hair wavesetting lotion or hair lacquer, which contains at least one resin conventionally used in wavesetting lotions or hair lacquers in alcoholic aqueous alcoholic solution.

7. A composition according to claim 6, which contains from 20 to 70% by weight of a low molecular weight alcohol having 1 to 6 carbon atoms.

8. A composition according to claim 6 or 7 which contains from 1 to 3% by weight of cosmetic resin.

9. A composition according to any one of claims 6 to 8, in which the resin is polyvinylpyrrolidone, a copolymer of crotonic acid and vinyl acetate, a copolymer of vinylpyrrolidone and vinyl acetate or a copolymer of maleic anhydride and butyl vinyl ether.

10. A composition according to any one of the preceding claims in which R represents a methyl group.

11. A composition according to any one of the preceding claims in which R'₁₀ represents a hydrogen atom or a methyl group.

12. A composition according to any one of the preceding claims in which R' represents a hydrogen atom or a methyl or —CN group.

13. A composition according to any one of the preceding claims in which R' represents a hydrogen or chlorine atom or a methyl group.

14. A composition according to any one of the preceding claims in which R' represents a hydrogen atom or a methyl or —CN group.

15. A composition according to any one of the preceding claims in which R' represents a hydrogen atom or a methyl, ethyl or β-hydroxyethyl group.

16. A composition according to any one of the preceding claims in which R' represents a hydrogen atom or a methyl, ethyl, β-hydroxyethyl or phenyl group.

17. A composition according to any one of the preceding claims in which at least one of R' and R' represents a hydrogen atom or a methyl or methoxy group.

18. A composition according to any one of the preceding claims in which at least one of R' and R' represents a hydrogen or chlorine atom or a methyl, nitro or acetyl-amino group.

19. A composition according to any one of claims 1 to 16 in which R' and R' together form, with the carbon atoms to which they are attached, a hydroxy-substituted benzene ring.

20. A composition according to any one of the preceding claims in which Z⁻ is a halide, fluoborate, perchlorate, sulphate or acetate.

21. A composition according to claim 20 in which Z⁻ is a methosulphate.

22. A composition according to any one of the preceding claims which additionally contains at least one anionic, cationic, non-ionic, amphoteric or zwitterionic surface-active agent, oxidising agent, synergistic agent or foam stabiliser, sequestering agent, superfatting agent, thickener, preservative, dispersing agent, swelling agent, penetrating agent, emollient or perfume.

23. A composition according to claim 1 substantially as hereinbefore described.

24. A composition according to claim 1 substantially as described in any one of Examples I to XXV.

25. A compound of formula (II) as defined in claim 1 in which R'₁₀, R', R', R', R', R', R', R', R and Z⁻ are as defined in claim 1 with the proviso that at least one of R' and R' represents a cyano group.

26. A compound of formula (II) as defined in claim 1 in which R' and R' do not represent a cyano group and R' and R' together with the carbon atoms to which they are attached form an unsaturated 6-membered ring carrying a hydroxyl substituent, chelated with a nitrogen atom of the azo group, in which case R', R', R' and R' each represents a hydrogen atom, and R'₁₀, R', R and Z⁻, and also R' and R', subject to the above proviso, are as defined in claim 1.

27. A compound according to claim 25 which has one or more of the features of claims 10, 11, 13, 15, 16 to 21.

28. A compound according to claim 26 which has one or more of the features of claims 10 to 14 and 19 to 21.

29. 4' - Amino - 8' - hydroxy - naphthalene - 1':2 - azo - 1 - methyl - pyridinium methosulphate.

30. 4' - Dimethylaminobenzene - 1':2 - azo - 4 - cyano - 1 - methyl - pyridinium methosulphate.

5 31. 4' - Bis(β - hydroxyethyl)aminobenzene - 1':2 - azo - 6 - cyano - 1,4 - dimethyl - pyridinium perchlorate. 5

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